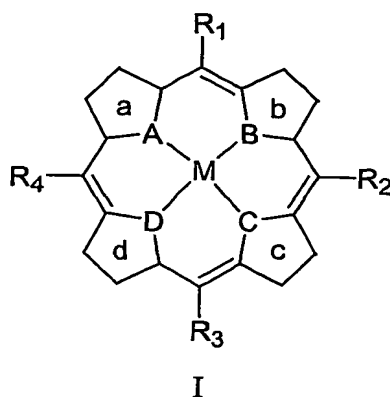


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CLAIMS

1. A compound of formula I, or a pharmaceutically acceptable salt thereof,



wherein

one or two of A, B, C and D are each independently selected from S, O, Se and Te, and the remainder are N;

a, b, c and d are each independently substituted or unsubstituted 5-membered heterocyclic groups having the members necessary to complete a porphyrin, chlorin, bacteriochlorin or isobacteriochlorin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te;

M is H or a metal;

R₁, R₂, R₃ and R₄ are each independently selected from:

H;

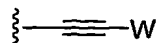
alkyl;

cycloalkyl;

halogen;

aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, COOH, COO-alkyl, -OZ, -COOZ, a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative,

-C≡C-(CH₂)_pCO₂R₁₀, where R₁₀ is H or alkyl, and O(CH₂)_rCOR₁₁, where R₁₁ is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;



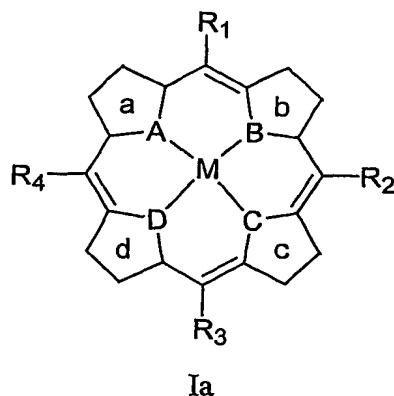
wherein W is an aryl, alkyl or heteroaryl group, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, haloalkyl, COOH, COO-alkyl, -OZ', -COOZ', a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH₂)_p-CO₂R₁₂, where R₁₂ is H or alkyl, and O(CH₂)_r-COR₁₃, where R₁₃ is OH, O-alkyl or N-succinimide, and p' and r' are each independently an integer from 1 to 10;

where Z and Z' are each independently silicon-containing protecting groups;

and wherein when a, b, c and d have the members necessary to complete a porphyrin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te,

- (a) R_1, R_2 and R_3 are identical, and $R_4 \neq R_1, R_2, R_3$; or
 (b) $R_1 = R_3$; $R_2 = R_4$, where $R_1, R_3 \neq R_2, R_4$; or
 (c) $R_2 = R_3$; $R_1 \neq R_4$; and $R_1, R_4 \neq R_2, R_3$.

2. A compound of formula Ia



wherein

one or two of A, B, C and D are each independently selected from S, O, Se and Te, and the remainder are N;

a, b, c and d are each independently substituted or unsubstituted 5-membered heterocyclic groups having the members necessary to complete a chlorin, bacteriochlorin or isobacteriochlorin nucleus in which one or two of the nitrogens are replaced by S, O, Se or Te;

M is H or a metal;

R₁, R₂, R₃ and R₄ are each independently selected from:

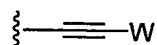
H;

alkyl;

cycloalkyl;

halogen;

aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, haloalkyl, COOH, COO-alkyl, -OZ, -COOZ, a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH₂)_pCO₂R₁₀, where R₁₀ is H or alkyl, and O(CH₂)_rCOR₁₁, where R₁₁ is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;



wherein W is an aryl, alkyl or heteroaryl group, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, haloalkyl, COOH, COO-alkyl, OZ', COOZ', a polyethylene glycol group, an alkyl sulfonate group, an alkyl-COOH group, a substituted or unsubstituted benzyl group, a sugar derivative, -C≡C-(CH₂)_pCO₂R₁₂, where R₁₂ is

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H or alkyl, and $O(CH_2)_rCOR_{13}$, where R_{13} is OH, O-alkyl or N-succinimide, and p' and r' are each independently an integer from 1 to 10;
 where Z and Z' are each independently silicon-containing protecting groups.

3. A compound according to claim 1 or claim 2 wherein one of A, B, C and D is S and the remainder are all N.

4. A compound according to any preceding claim wherein R_1 , R_2 , R_3 and R_4 are each independently selected from:

H;

halogen;

phenyl or pyridyl, each of which are optionally substituted by one or more substituents selected from OH, CN, CF_3 , alkyl, alkoxy, haloalkyl, halogen, NH_2 , NO_2 , $CONH_2$, haloalkyl, COOH, COO-alkyl, OZ, COOZ, a polyethylene glycol group, $-C\equiv C-(CH_2)_pCO_2R_{10}$, where R_{10} is H or alkyl, and $O(CH_2)_rCOR_{11}$, where R_{11} is OH, O-alkyl or N-succinimide, and p and r are each independently an integer from 1 to 10;

$\{ \text{---} \equiv \text{---} W$

wherein W is a phenyl or pyridyl group, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF_3 , alkyl, alkoxy, haloalkyl, halogen, NH_2 , NO_2 , $CONH_2$, haloalkyl, COOH, COO-alkyl, OZ', COOZ', a polyethylene glycol group, $-C\equiv C-(CH_2)_pCO_2R_{12}$, where R_{12} is H or alkyl, and $O(CH_2)_rCOR_{13}$, where R_{13} is OH, O-alkyl or N-succinimide, and p' and r' are each independently an integer from 1 to 10.

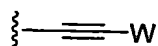
5. A compound according to any preceding claim wherein R_1 , R_2 , R_3 and R_4 are each independently selected from:

H;

halogen;

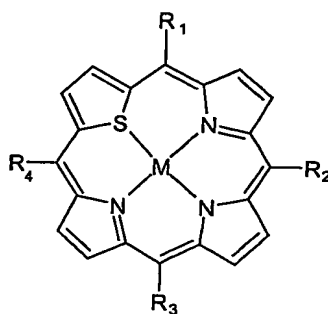
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phenyl or pyridyl, each of which are optionally substituted by one or more substituents selected from alkoxy, halogen, OH, $O(CH_2)_rCOR_{11}$ and $-C\equiv C-(CH_2)_pCO_2R_{10}$;



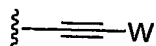
wherein W is phenyl or pyridyl, each of which may be optionally substituted by one or more substituents selected from OH, OZ' and a polyethylene glycol group.

6. A compound according to any one of claims 1, 3, 4 or 5 which is of formula II



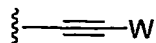
II

7. A compound according to claim 6 wherein
 R₁ and R₄ are different and are selected from aryl and heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, haloalkyl, COOH, COO-alkyl, OZ and COOZ; and
 R₂ and R₃ are the same and are both H, halogen or



8. A compound according to claim 7 wherein
 R₁ is aryl optionally substituted by an alkoxy group;
 R₂ and R₃ are both H, halogen or

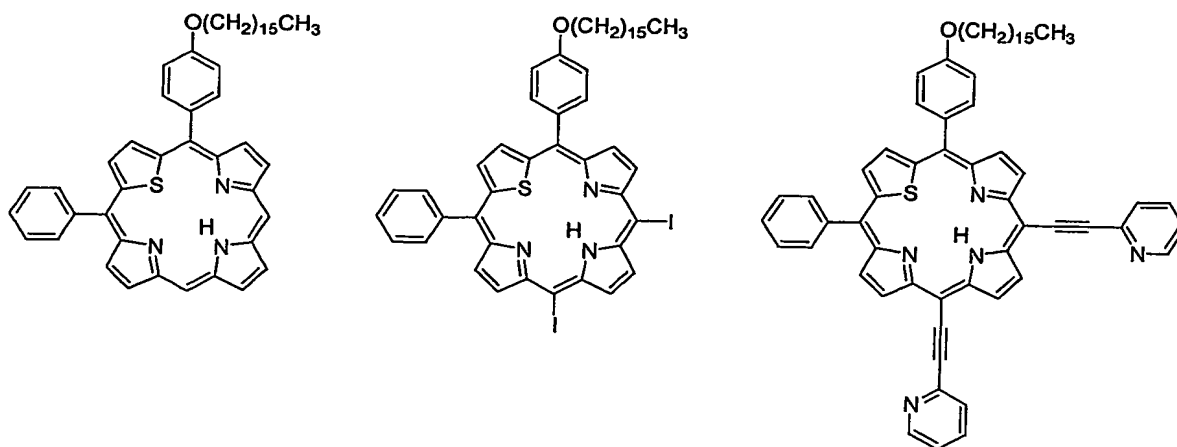
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where W is a pyridyl;

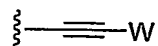
R₄ is phenyl.

9. A compound according to claim 8 which is selected from the following:



10. A compound according to claim 6 wherein

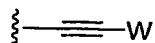
R₁ are R₃ are the same and are both H, halogen or



R₂ and R₄ are the same and are both aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

11. A compound according to claim 10 wherein

R₁ and R₃ are both H, halogen or

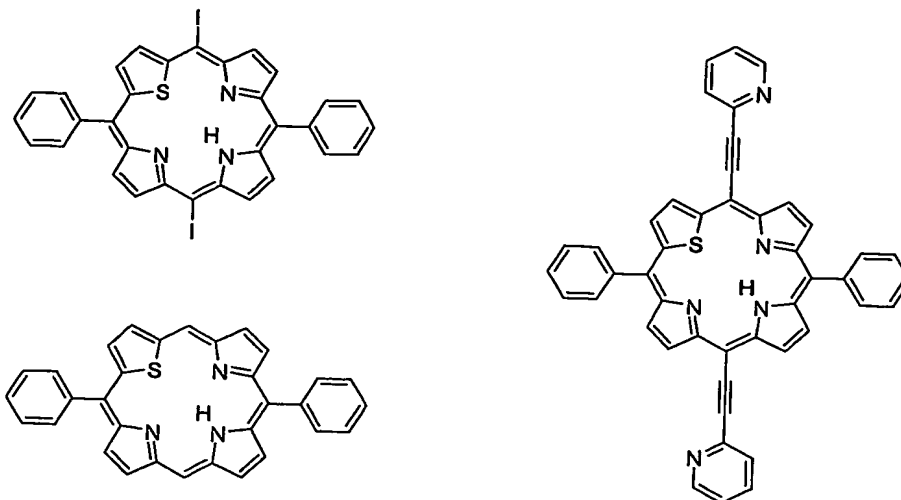


where W is pyridyl;

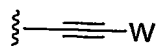
R₂ and R₄ are both phenyl.

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12. A compound according to claim 11 which is selected from the following:



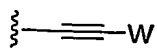
13. A compound according to claim 6 wherein
 R_1, R_2 and R_3 are the same and are all H, halogen or



R_4 is aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF_3 , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH_2 , NO_2 , $CONH_2$, haloalkyl, COOH, COO-alkyl, OZ, COOZ, $-C\equiv C-(CH_2)_pCO_2R_{10}$, where R_{10} is H or alkyl, and $O(CH_2)_rCOR_{11}$, where R_{11} is OH, O-alkyl or -N-succinimide, and p and r are each independently an integer from 1 to 10.

14. A compound according to claim 13 wherein

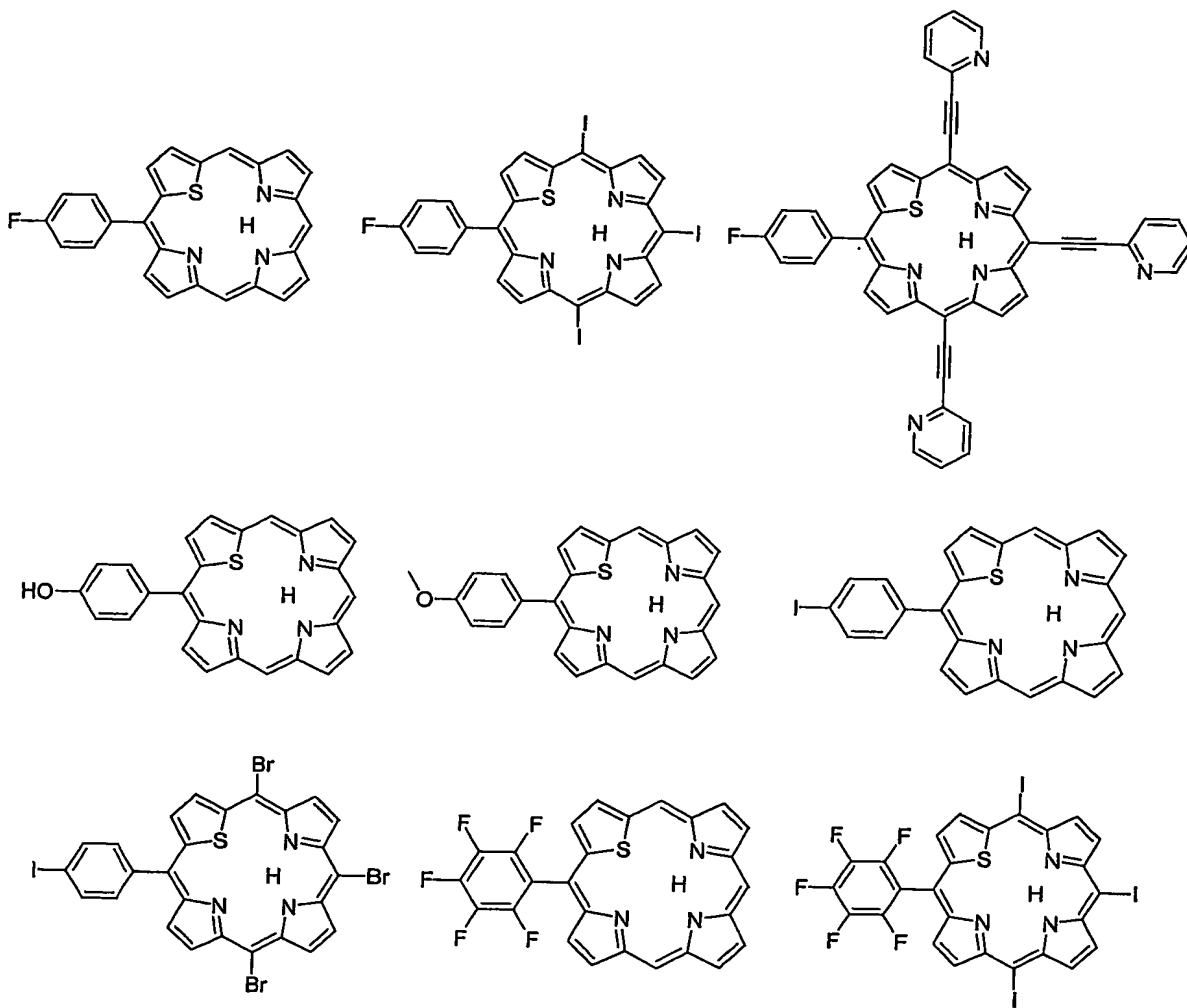
R_1, R_2 and R_3 are all H, halogen or



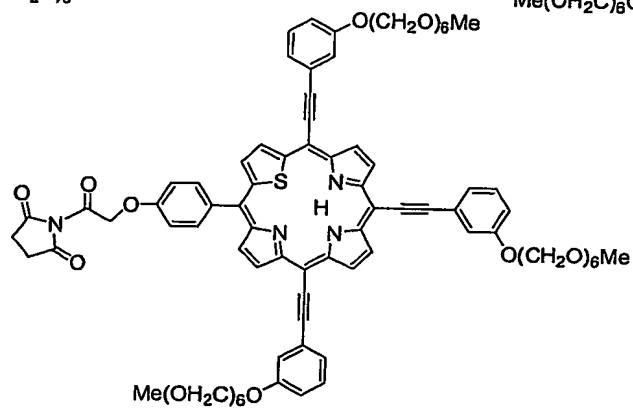
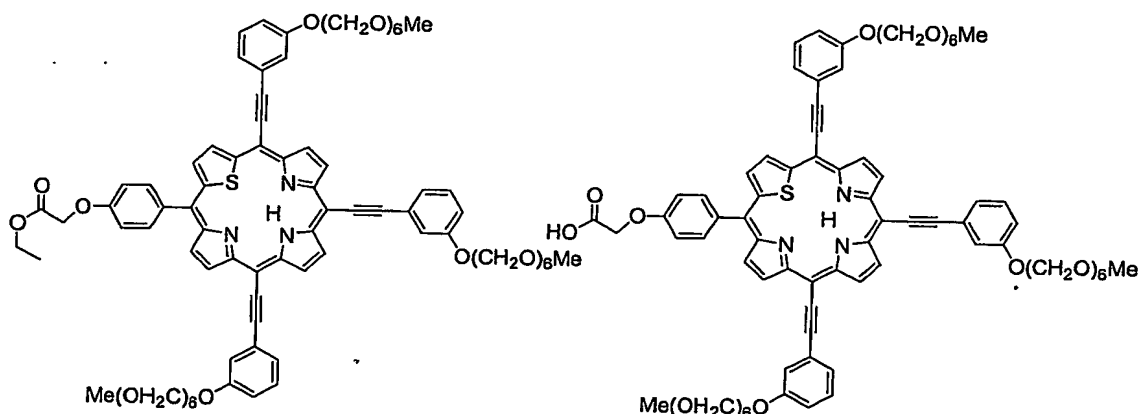
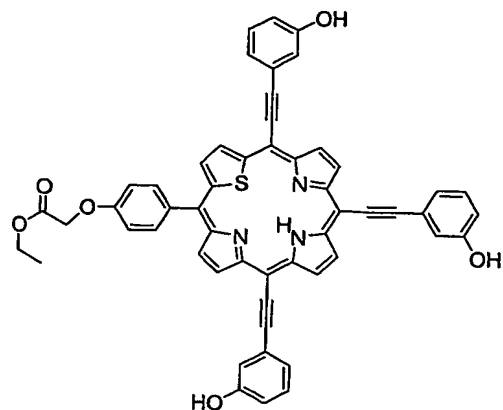
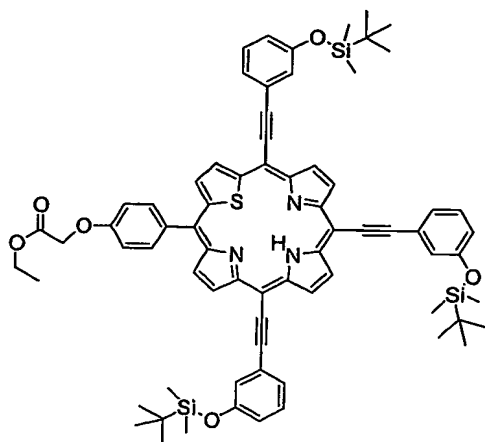
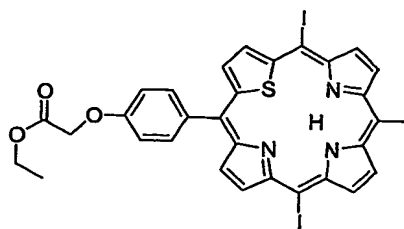
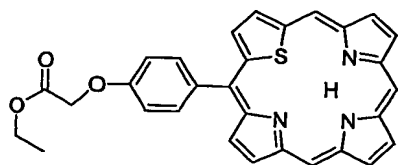
where W is a pyridyl or phenyl group, each of which may be optionally substituted by one or more substituents selected from OH, OZ', and a polyethylene glycol group; and
 R_4 is a phenyl group substituted by one or more halogen, alkoxy, $O(CH_2)_pCOR_{11}$ or $-C\equiv C-(CH_2)_pCO_2R_{10}$ groups.

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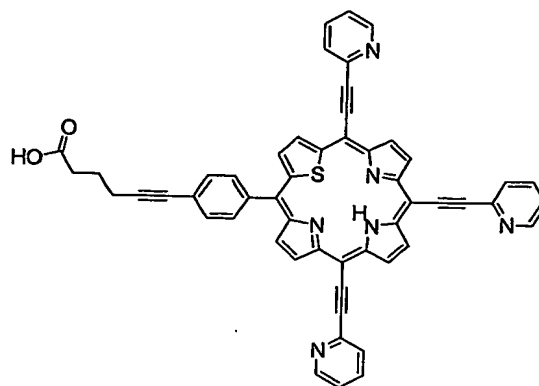
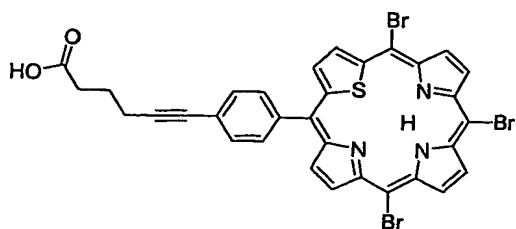
15. A compound according to claim 14 wherein said compound is selected from the following:



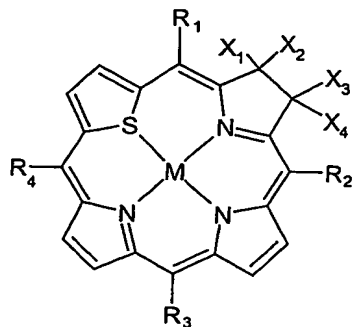
84



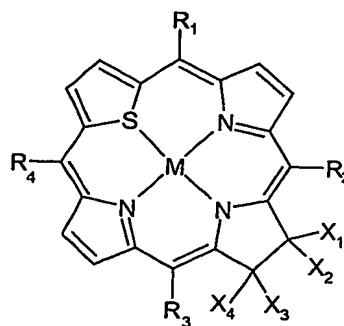
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16. A compound according to any one of claims 1 to 5 which is of formula III or IV



III

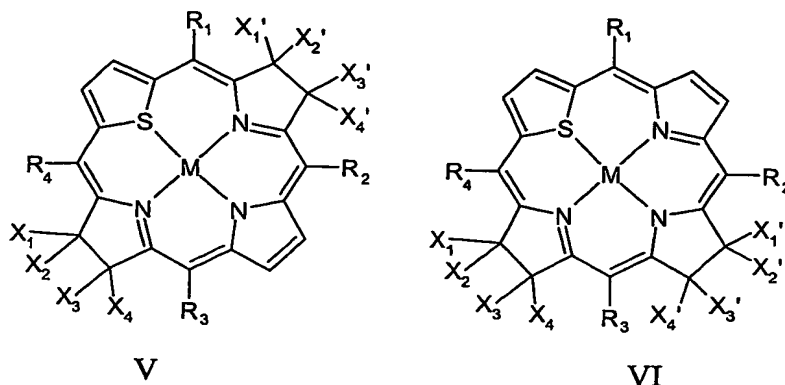


IV

wherein X₁-X₄ are each independently selected from H, OH, alkyl, alkoxy; or C=O, where X₂ and X₄ respectively are absent, and R₁-R₄ and M are as defined in claim 1.

17. A compound according to claim 16 wherein X₁ and X₃ are OH, and X₂ and X₄ are H.

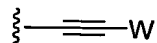
18. A compound according to any one of claims 1 to 5 which is of formula V or VI



wherein R_1 - R_4 and M are as defined in claim 1, and X_1 - X_4 and X_1' - X_4' are each independently selected from H, OH, alkyl, alkoxy; or C=O, where X_2 , X_4 , X_2' and X_4' respectively are absent.

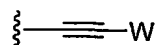
19. A compound according to claim 18 wherein X_1 , X_3 , X_1' and X_3' are OH, and X_2 , X_4 , X_2' and X_4' are all H.

20. A compound according to claim 16 or claim 18 wherein R_1 , R_2 and R_3 are the same and are all H, halogen or



R_4 is aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF_3 , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH_2 , NO_2 , CONH_2 , haloalkyl, COOH , COO-alkyl , OZ and COOZ .

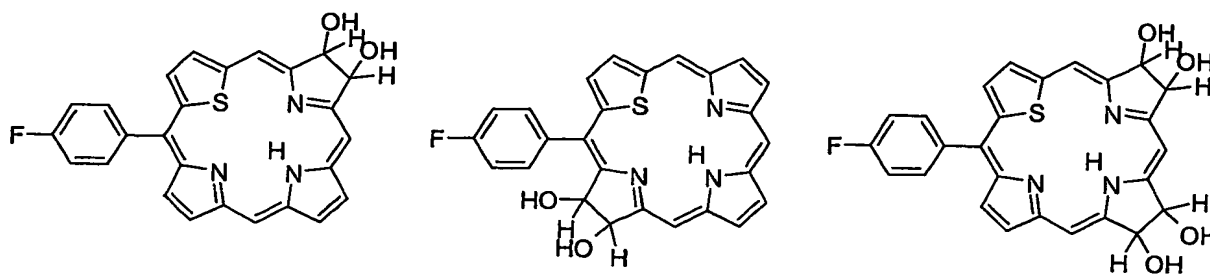
21. A compound according to claim 20 wherein R_1 , R_2 and R_3 are all H, halogen or



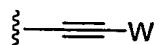
where W is pyridyl; and

R₄ is a halogen substituted aryl group.

22. A compound according to claim 21 which is selected from:



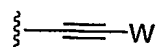
23. A compound according to claim 16 or claim 18 wherein
R₂ and R₃ are the same and are both H, halogen or



R₁ and R₄ are different and are aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF₃, alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH₂, NO₂, CONH₂, haloalkyl, COOH, COO-alkyl, OZ and COOZ.

24. A compound according to claim 23 wherein

R₂ and R₃ are both H, halogen or

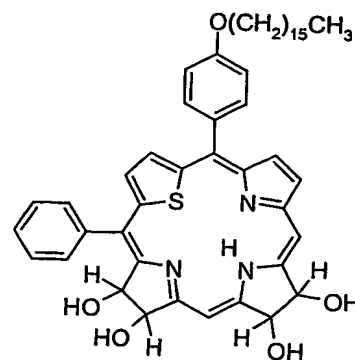
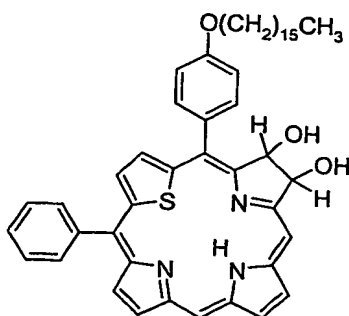
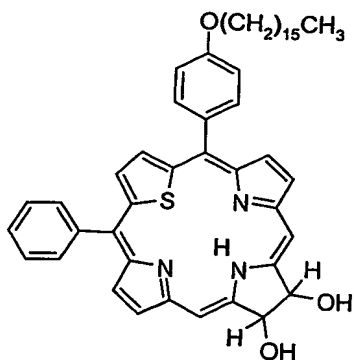


where W is pyridyl;

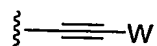
R₄ is phenyl; and

R₁ is alkoxy substituted phenyl.

25. A compound according to claim 24 which is selected from:



26. A compound according to claim 16 or claim 18 wherein
 R_1 and R_3 are the same and are both aryl or heteroaryl, each of which may be optionally substituted by one or more substituents selected from OH, CN, CF_3 , alkyl, alkoxy, haloalkyl, halogen, an isothiocyanate group, a haloacetamide, maleimide, NH_2 , NO_2 , $CONH_2$, haloalkyl, $COOH$, COO -alkyl, OZ and $COOZ$; and
 R_2 and R_4 are the same and are both H, halogen or



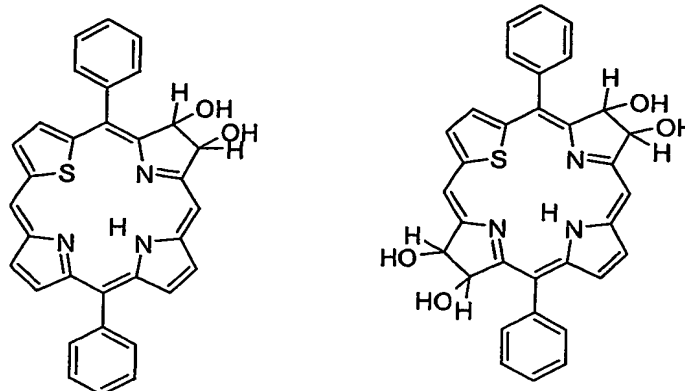
27. A compound according to claim 26 wherein

R_1 and R_3 are both phenyl; and

R_2 and R_4 are both H.

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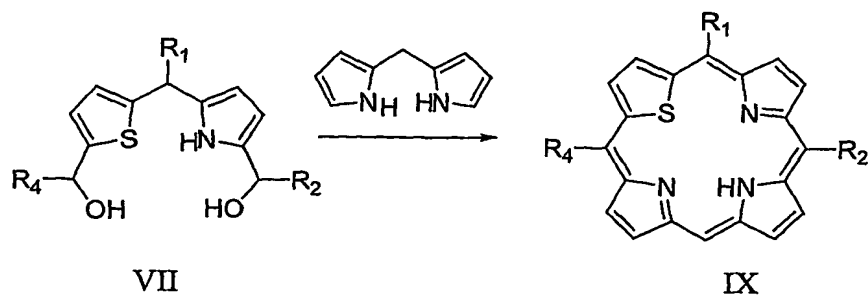
28. A compound according to claim 27 which is selected from the following:



29. A compound according to any preceding claim wherein M is selected from H, Ni, Pb, V, Pd, Co, Nb, Al, Sn, Zn, Cu, Mg, Ca, In, Ga, Fe, Eu, Lu, Pt, Ru, Mn and Ge.
30. A compound according to any preceding claim wherein M is H or Zn.
31. A pharmaceutical composition comprising a compound according to any one of claims 1 to 30 admixed with a pharmaceutically acceptable diluent, excipient or carrier.
32. A conjugate molecule comprising a compound as defined in any one of claims 1 to 30 and a targeting moiety selected from a recombinant antibody, a Fab fragment, a F(ab')₂ fragment, a single chain Fv, a diabody, a disulfide linked Fv, a single antibody domain and a CDR.
33. A conjugate molecule which comprises a polypeptide carrier comprising at least one alpha helix having synthetically attached thereto a plurality of compounds as defined in any one of claims 1 to 30.
34. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33 in medicine.

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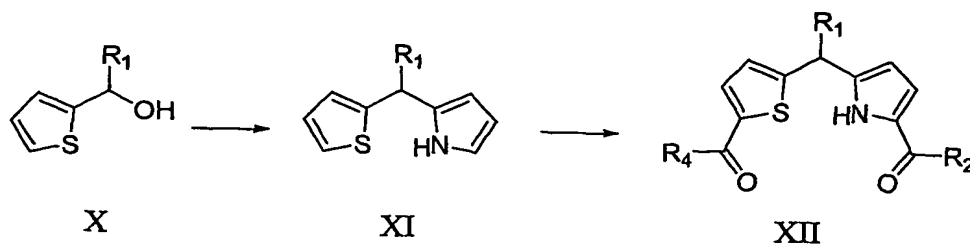
35. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, for medical imaging.
36. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, in the preparation of a medicament for photodynamic therapy.
37. Use of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33, in the preparation of a medicament for treating a proliferative disorder.
38. Use of a compound according to any one of claims 1 to 30 in the preparation of a conjugate according to claim 32 or claim 33.
39. A method of treating a proliferative disorder, said method comprising administering to a subject a therapeutic amount of a compound according to any one of claims 1 to 30, or a conjugate according to claim 32 or claim 33.
40. A process for preparing a compound as defined in claim 1 or claim 2, said process comprising reacting a compound of formula VII with a dipyrrole to form a compound of formula IX



where R₁, R₂ and R₄ are as defined in claim 1.

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41. A process according to claim 40 wherein said compound of formula VII is prepared via intermediates X, XI and XII



42. A process according to claim 40 or claim 41 for preparing a compound according to claim 17 or claim 19 which further comprises oxidising said compound of formula IX with osmium tetroxide.